

CLAIMS

1. An automatic dishwasher detergent formulation comprising: -

(a) a metal complex compounds of formula (1)



wherein Me is manganese, titanium, iron, cobalt, nickel or copper,

X is a co-ordinating or bridging radical,

n and m are each independently of the other an integer having a value of from 1 to 8,

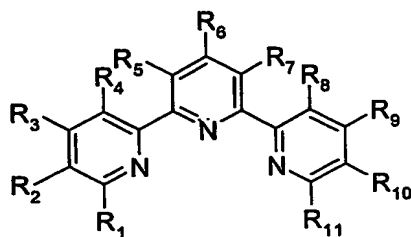
p is an integer having a value of from 0 to 32,

z is the charge of the metal complex,

Y is a counter-ion,

q = z/(charge Y), and

L is a ligand of formula



(2)

wherein

R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀ and R₁₁ are each independently of the others hydrogen; unsubstituted or substituted C₁-C₁₈alkyl or aryl; cyano; halogen; nitro; -COOR₁₂ or -SO₃R₁₂ wherein R₁₂ is in each case hydrogen, a cation or unsubstituted or substituted C₁-C₁₈alkyl or aryl; -SR₁₃, -SO₂R₁₃

or $-OR_{13}$ wherein R_{13} is in each case hydrogen or unsubstituted or substituted C_1-C_{18} alkyl or aryl; $-N(R_{13})-NR'_{13}R''_{13}$ wherein R_{13} , R'_{13} and R''_{13} are as defined above for R_{13} ; $-NR_{14}R_{15}$ or $-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{14} , R_{15} and R_{16} are each independently of the other(s) hydrogen or unsubstituted or substituted C_1-C_{18} alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom bonding them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms; with the proviso that R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} and R_{11} are not simultaneously hydrogen, as a catalyst for oxidation reactions; and

(b) an enzyme.

2. A formulation according to claim 1, wherein Me is manganese which is present in oxidation state II, III, IV or V.

3. A formulation to either claim 1 or claim 2, wherein X is CH_3CN , H_2O , F^- , Cl^- , Br^- , HOO^- , O_2^{2-} , O^{2-} , $R_{17}COO^-$, $R_{17}O^-$, $LMeO^-$ or $LMeOO^-$ wherein R_{17} is hydrogen or unsubstituted or substituted C_1-C_{18} alkyl or aryl, and L and Me are as defined in claim 1.

4. A formulation according to any one of claims 1 to 3, wherein Y is $R_{17}COO^-$, ClO_4^- , BF_4^- , PF_6^- , $R_{17}SO_3^-$, $R_{17}SO_4^-$, SO_4^{2-} , NO_3^- , F^- , Cl^- , Br^- or I^- wherein R_{17} is hydrogen or unsubstituted or substituted C_1-C_{18} alkyl or aryl.

5. A formulation according to any one of claims 1 to 4, wherein n is an integer having a value of from 1 to 4, especially 1 or 2.

6. A formulation according to any one of claims 1 to 5, wherein m is an integer having a value of 1 or 2, especially 1.

7. A formulation according to any one of claims 1 to 6, wherein p is an integer having a value of from 0 to 4, especially 2.

8. A formulation according to any one of claims 1 to 7, wherein z is an integer having a value of from 8- to 8+.

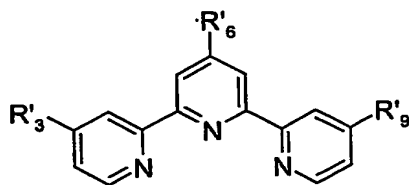
9. A formulation according to any one of claims 1 to 8, wherein aryl is phenyl or naphthyl unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy.

10. A formulation according to any one of claims 1 to 9 wherein the 5-, 6- or 7-membered ring formed by R_{14} and R_{15} together with the nitrogen atom bonding them is an unsubstituted or C_1 - C_4 alkyl-substituted pyrrolidine, piperidine, piperazine, morpholine or azepane ring.

11. A formulation according to any one of claims 1 to 10, wherein R_6 is C_1 - C_{12} alkyl; phenyl unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, cyano, nitro, carboxyl,

sulfo, hydroxyl, amino, N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy; cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation, C_1 - C_{12} alkyl, or phenyl unsubstituted or substituted as indicated above; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen, C_1 - C_{12} alkyl, or phenyl unsubstituted or substituted as indicated above; $-N(R_{13})-NR'_{13}R''_{13}$ wherein R_{13} , R'_{13} and R''_{13} are as defined above for R_{13} ; $-NR_{14}R_{15}$ or $-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{14} , R_{15} and R_{16} are each independently of the other(s) hydrogen, unsubstituted or hydroxyl-substituted C_1 - C_{12} alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom bonding them form an unsubstituted or C_1 - C_4 alkyl-substituted pyrrolidine, piperidine, piperazine, morpholine or azepane ring; and R_1 , R_2 , R_3 , R_4 , R_5 , R_7 , R_8 , R_9 , R_{10} and R_{11} are as defined above or are hydrogen.

12. A formulation according to claim 11, wherein the ligand L is a compound of formula



(3)

wherein

R'_3 , R'_6 and R'_9 are as defined for R_6 in claim 11.

13. A formulation according to claim 12, wherein

R'_3 , R'_6 and R'_9 are each independently of the others C_1 - C_4 alkoxy; hydroxy; phenyl unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, phenyl or by hydroxy; hydrazino; amino;

N-mono- or N,N-di-C₁-C₄alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety; or an unsubstituted or C₁-C₄alkyl-substituted pyrrolidine, piperidine, piperazine, morpholine or azepane ring.

14. A formulation according to claim 13, wherein R₆ is hydroxy.

15. A formulation according to claim 14, wherein a metal complex compound of formula (1) is formed *in situ* in the dishwashing operation.

16. A formulation according to any one of claims 1 to 15, wherein the enzyme is a protease.

17. A formulation according to any one of claims 1 to 16, wherein the enzyme is separated from a component of the formulation.

18. A formulation according to claim 17 wherein the enzyme is encapsulated.

19. A formulation according to any one of claims 1 to 18, wherein the metal complex compounds of formula (1) is a bleach activation catalyst.

20. A formulation according to claims 19, wherein the formulation comprises an additional bleach-activating component.

21. A formulation according to any one of claims 1 to 20, wherein the formulation comprises a builder.

22. A formulation according to any one of claims 1 to 21, wherein the formulation comprises a surfactant.

23. A formulation according to claim 22, wherein the surfactant is a nonionic low sudsing surfactant.

24. A formulation according to any one of claims 1 to 23, wherein the formulation comprises an oxygen source.

25. A formulation according to claim 24, wherein the oxygen source is perborate, percarbonate, hydrogen peroxide or a mixture thereof.

26. An automatic dishwasher detergent formulation, containing

- I) 0 - 30%, preferably 0 - 10%, of a surfactant,
- II) 0 - 90%, preferably 0 - 70%, of a builder / co-builder,
- III) 1 - 99%, preferably 1 - 50 %, of a peroxide or a peroxide-forming substance, and
- IV) a metal complex compound of formula (1) in an amount which, in the liquor, gives a concentration of 0.5 - 200 mg/litre of liquor, when from 0.5 to 20g/litre of the dishwashing formulation are added to the liquor.

27. A formulation according to any one of claims 1 to 26, wherein the formulation is in the form of a tablet.

28. Use of a formulation according to any one of claims 1 to 27 in an automatic dishwasher.